Research Article

Efficient Recovery of Trapped Phosphorus from Waste Phosphogypsum of a Phosphoric Acid Plant

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Abstract

Methods for efficient recovery of trapped phosphorous from phosphogypsum using leaching reagents are investigated. The recovery of phosphorous in final product is evaluated and provided recommendations for the application of recovered phosphorous in acid processes and treated gypsum in other applications. The dissolution was carried out by studying four variables namely, concentration, interaction time, solid to liquid ratio and temperature. The obtained leachate and treated solid gypsum were analysed for their phosphorous content and other impurities. The result indicates that dilute sulphuric acid can effectively recover phosphorous from waste phosphogypsum. With the optimum leaching conditions like 4% concentration and stirring time of 180 min., maximum recovery of phosphorous can be achieved. Effective recovery of P_2O_5 from phosphogypsum can increase phosphoric acid production efficiency of the wet phosphoric acid plant.

Keywords: Phosphogypsum, Phosphoric Acid, Processing Methods, Rock Phosphate, Recycling, Recovery, Waste Treatment

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Introduction

Phosphorus is a primary essential plant nutrient and a building block in food production. Agriculture sector uses great amount of phosphorous containing fertilizers that growing plants take up from the soil [1]. Most of the phosphorous is being utilized as a principle component of macronutrient nitrogen-phosphorous-potassium containing fertilizers. The primary raw material which is being used in the production of phosphorous based fertilizer is Phosphoric Acid. The phosphoric acid is produced using the rock phosphate which is the naturally occurring source for P_2O_5 and the phosphate rock minerals are the only significant global resources of phosphorous [2].

Phosphogypsum is an acidic by-product produced by the phosphatic fertilizer industry during the production of phosphoric acid from phosphate rock through wet process [3]. About 2 % of P_2O_5 is generally retained by this phosphogypsum along with some levels of fluoride, certain natural-occurring radionuclides and trace elements [4].

For the production of phosphoric acid, the wet process is most frequently used, in which the finely grounded phosphate rock is dissolved in phosphoric acid to form the slurry of monocalcium phosphate. Further sulphuric acid is added to the slurry to produce phosphoric acid. In this process acidic phosphogypsum is formed as a by-product. The chemical scheme of the process is given as below Equations (1-3) [5].

$$Ca_{10}F_2(PO_4)_6 + 14H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2HF \quad (1)$$

$$Ca(H_2PO_4)_2 + H_2SO_4 + 2H_2O \rightarrow 2H_3PO_4 + CaSO_4.2H_2O \quad (2)$$

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4.2H_2O + 2HF \quad (3)$$

During this wet process of phosphoric acid production, about 4.5 to 5 Tonnes of phosphogypsum is generated per tonne of phosphoric acid produced [6] which also depends on the source of rock phosphate used in the process. The generated acidic phosphogypsum in a slurry form is mixed with water and then transported to a dedicated large facility- phosphogypsum holding pond. In the phosphogypsum pond, the solid particles of phosphogypsum are allowed to settle down for few days and the water from the slurry is decanted and used as process water.

Around the world, only 15% of the produced phosphogypsum is recycled as an agricultural fertilizer while the remaining 85% is not being utilized efficiently [7]. In India, different states such as Andhra Pradesh, Gujarat, Kerala, Maharashtra, Orissa, Tamil Nadu and West Bengal has phosphoric acid production units and large amount of phosphogypsum is produced from these phosphoric acid industries [8].

From the analysis of phosphogypsum conducted during this study, it is evident that, about 2% of P_2O_5 stays trapped with the by-product phosphogypsum after the phosphoric acid production. Considering the huge volumes of

phosphogypsum being produced by the phosphoric acid plants, total quantity of P_2O_5 staying unused in the acid production system is considerably high. Recovery of this P_2O_5 from the phosphogypsum back into the process can significantly increase the production efficiency which intern will improve the quality and yield of the phosphoric acid. Along with this, phosphogypsum also contains several valuable components such as calcium sulphate, natural radioactive elements, fluorides and sulphate and other rare earth elements such as silicon, iron, titanium, magnesium, aluminium, and manganese, as well as toxic elements such as heavy metals and other rare earth elements [9, 10].

Different processes are being used for the recovery of phosphorous as well as removing other impurities like heavy metal and rare-earth elements from phosphogypsum. These processes are water washing, thermal, and chemical treatments applied to the phosphogypsum sludge. It has been reported that water-soluble impurities can be removed by washing with water, whereas HPO_4^{2-} and FPO_3^{2-} substituted in the crystal lattice of gypsum with SO_4^{2-} ions form solid solutions and difficult to be removed by washing. The heavy metals and other rare-earth elements present in the phosphogypsum can be removed by treating it with various acids and reagents [11]. It is also reported that both organic and inorganic acids can extract trapped phosphorous from phosphogypsum [12].

Various methods are available to recover impurities and phosphorous from phosphogypsum. Using nitric acid for treating phosphate has been studied and found to be an acceptable route. Comprehensive studies on rate earth element recovery were performed using nitric acid extraction method and the nitric acid solution resulted from leaching was containing phosphorous, rare-earth metals, also contains calcium, aluminium, and iron impurities [13, 14]. Different methods have been suggested to remove impurities and for the extraction of phosphorous from phosphogypsum, by treating it with Sulphuric acid [15], ammonium hydroxide [16], hot ammonium sulphate solution [17], diluted hydrochloric acid [18], citric acid [19] and acetic acid [20], as leaching reagents.

In the present study, leaching experiments were carried out using sulphuric acid as inorganic extracting reagent for phosphorous recovery from phosphogypsum. The main aim of this study was to recover maximum phosphorous from phosphogypsum in the phosphoric acid production process, where sulphuric acid is one of the raw material. Based on the study performed for purification of phosphogypsum and recovery of rare earth elements from phosphogypsum, sulphuric acid solutions of medium concentrations has shown that recovery has been successfully achieved [21]. The investigation on the reduction of phosphorous was carried out and sulphuric acid proved to be the best inorganic extracting agent for the recovery of phosphorous [22]. The effect of parameters such as temperature and agitation time are yet to be studied for the recovery in aqueous filtrate solution and dried phosphogypsum after treatment through the characterization. A promising process for the recovery of phosphorous from phosphogypsum is hence a requirement.

In a typical plant of capacity of 200MT phosphoric acid productions, about 1000 ton of phosphogypsum is produced as by-product. Hence, based on analysis of phosphogypsum 13MT of P_2O_5 goes unused in waste phosphogypsum. Even if we could recover 50% of this P_2O_5, overall utilization efficiency of P_2O_5 in phosphoric acid production process can be increased.

In addition to this, after purifying phosphogypsum using several techniques, it can be utilized for various applications such as installing captive plaster, gypsum board manufacturing units, cement manufacturing units, manufacture of ammonium sulphate, recovery or manufacturing of sulphuric acid and road making [23].

Experimental

In a wet process of phosphoric acid production, the by-product phosphogypsum slurry, which is getting produced in the agitation tank is pumped to phosphogypsum stack area through a rubber lined steel pipeline. Additional pipeline is installed to pump back decanted water from phosphogypsum stack. In the further process, distribution of water and solid phosphogypsum occurs through peripheral rim ditches. The solid phosphogypsum settles down due to gravity and higher weight, while the water stays on the top. This water is then decanted by flowing it down with the use of gravity to the water holding ponds. From these surge tanks, it is pumped back for reuse in phosphoric acid plant as process water. In some processes plants uses filtration process to separate phosphogypsum from the water in which the Phosphogypsum is removed as dry cake and transported to the disposal area by conveyor belt or any other means of solids handling systems. However, this process is not extensively used as slurry pumping process is simpler and less expensive.

Sample collection for phosphogypsum leaching experiments

To recover phosphorous and removing impurities from dry phosphogypsum and decanted water from phosphogypsum stack, leaching experiments were performed. For these, samples of phosphogypsum from different locations of gypsum pond facility of GSFC, Vadodara were collected. Procedure for sampling was followed as collecting a sample upto a depth of 0.50 m beneath the surface for every grid size of 250×250 m upto a radius of 500 m from the edge of

the phosphogypsum stack [23]. Samples of rock phosphate used in the manufacturing process of phosphoric acid were also collected for the analysis.

Composition and properties of phosphogypsum

The quality and composition of the phosphogypsum depends upon the quality of the raw materials used in the manufacturing process and the process route used to produce phosphoric acid [24]. The phosphate rock used in the phosphoric acid production at GSFC is either procured from Udaipur or imported from Tunisia and Jordan. Phosphogypsum is a usually a grey, damp, fine grained powdered material.[24] The moisture content is in the range of 8–30% [25]. The moisture content in the sample was tested and found 25.26%. Phosphogypsum contains impurities such as free phosphoric acid, phosphates, fluorides and organic matter [26]. The data presented by the International Atomic Energy Agency (IAEA) [25] shows high SO_4, CaO, SiO_2 and P_2O_5 contents in phosphogypsum. Phosphogypsum consists primarily of calcium sulphate dihydrate with small amounts of silica usually as quartz, aluminum, iron and unreacted phosphate rock, traces of radioactive material (like uranium), traces of heavy metals like mercury, arsenic, lead, nickel, cobalt, chromium and it also contains some amount for fluoride.[15] Uranium was tested in the sample where it was not traceable.

Tunisian phosphogypsum obtained comprises 90% bassinettes, 9% gypsum and 1% Brucite [24]. The analytical data of phosphate rock presented in the paper shows details regarding contents of phosphate rock obtained from Udaipur.

Impurity profile of treated phosphogypsum with sulphuric acid

Phosphogypsum contains considerable amounts of rare-earth elements [27]. The concentration of these elements depends on the composition of the phosphate rock. Different studies have been carried out for recovery of impurities from phosphogypsum [28]. The leaching method that has been followed in this study is useful in recovery of these elements. **Table 1** represents the analytical data of heavy metals and radioactive element in leaching solution from the extraction experiments. From the analytical data presented, it is evident that nickel and cobalt are being recovered in leachate using 4% sulphuric acid solution. The activities and concentrations of different radio-active elements in phosphogypsum vary with the origin of the rock used in the phosphate industry. The resultant raw material phosphogypsum is enriched with radioactive elements. The source of radioactivity comes mainly from ^{238}U and ^{232}Th [29]. The radiation dose affecting because of the phosphogypsum stacks is negligible compared to the average annual effective dose from natural sources of radioactivity [30]. Along with this, the radiation dose affecting by phosphogypsum used in plaster or construction material is also negligible [31, 32].

Table 1 Extraction of impurities into leaching solution obtained after treating phosphogypsum with 4% H_2SO_4 solution

Trace element	Hg	As	Pb	Ni	Co	Cr
Content (ppm)	NT	NT	NT	0.415	0.046	NT
Radio-nuclide	Uranium – NT					
*NT: Not Traced						

Analysis and equipments

The collected samples for this study were analysed and their characterization is done using standard test procedures.

- pH was measured using pH analyser.
- Density was measured using density bottle and specific gravity was measured using Hydrometer.
- Uranium analysis was done through ICPMS analysis.
- Moisture content was determined using oven drying method.
- Other elements were determined by Atomic Absorption Spectroscopy.
- P_2O_5 was analysed gravimetrically.

Analytical testing of rock phosphate, raw phosphogypsum and water from phosphogypsum stack

The samples of the raw material rock phosphate, by-product phosphogypsum and decanted water from phosphogypsum stack were analysed prior to leaching experiments to understand the amount of phosphorous recovery after extractions and impurity profile. The analytical data is represented in the following **Tables 2** and **3**.

The content of rare-earth metals and major impurity components in phosphogypsum and water from phosphogypsum stack are given in **Table 4** and **5**. The concentrations of these metals contents depend on the composition of the phosphate rock. Hence, analysis of rock phosphate was also conducted. Analytical data for the same is given in **Table 6**.

Table 2 Chemical composition of phosphogypsum

Parameters	Moisture	Phosphorous (As P_2O_5)	P_2O_5 (Dry basis)	Fe_2O_3	Al_2O_3	Fluoride
Content	25.26%	1.32%	1.77%	0.44%	1.39%	105 ppm

Table 3 Analytical data of water from phosphogypsum stack

Parameters	Density	P2O5	Sulphate	Fluoride
Content	1.02 g/cc	0.56%	5.022%	106 ppm

Table 4 Main rare earth elements and heavy metals in phosphogypsum

Trace element	Hg	As	Pb	Ni	Co	Cr
Content (ppm)	NT	NT	0.073	14.48	7.7	2.73
Radio-nuclide	Uranium – NT					
*NT: Not Traced						

Table 5 Main rare earth elements and heavy metals in water from phosphogypsum stack

Trace element	Hg	As	Pb	Ni	Co	Cr
Content (ppm)	NT	NT	NT	NT	0.06	NT
Radio-nuclide	Uranium – NT					
*NT: Not Traced						

Table 6 Composition of the phosphate rock

Parameter	LOI	Acid Insoluble	SiO_2	CaO	P_2O_5	F	Fe_2O_3	Al_2O_3	Na_2O	K_2O	SO_3	CO_2	CO	Mg
Content (%)	3.04	10.2	9.51	46.3	32.48	2.87	2.22	0.41	0.19	0.07	0.05	2.24	8.85	0.45

Leaching experiments with sulphuric acid

Sulphuric Acid of 98% strength (product of GSFC plant) is used as extracting regent to recover remaining phosphorous in phosphogypsum. Based on the initial analysis of water from gypsum pond, it is evident that it contains some amount of phosphorous which ensures its recovery if used in an extracting process. The effect of sulphuric acid as leaching reagent for recovery of P_2O_5 from Phosphogypsum is determined by investigating variables such as phosphogypsum quantity: 100 g, 75 g, 50 g; phosphogypsum to acid ratio- 100:100, 75:100, 50:100; acid concentration: 2%, 4% & 8%; reaction time: 60 min., 120 min. & 180 min. Considering this, experiments were designed as per Table 6. Percentage of P_2O_5 recovered from phosphogypsum is calculated using its estimated absolute values in the residue compare to initial phosphogypsum used.

Various leaching conditions were used during the series of experiments. Sulphuric acid solutions of different strengths like 2 %, 4 % and 8% were prepared and kept in stock. Series of experiments were conducted by taking predefined quantities of phosphogypsum into 250 ml beaker and then predefined quantities of sulphuric acid solution are added to it as mentioned in **Table 7**. The compositions were kept at room temperature. Continuous stirring was applied using a magnetic stirrer for pre-determined time (1 hour, 2 hour or 3 hour). After conducting the leaching experiment, the slurry was filtered and residue was washed with water from phosphogypsum pond. Then the whole material was transferred to a filter assembly with a Buchner funnel having a pre-weighed Whatman Filter paper No.1 (pore size: 11µm) placed in it. Slight vacuum suction is applied to the filtration flask for 5 minutes. The collected residue solids were dried at 42°C for 24 h and weighed [17]. The dried residue and the filtrate were stored separately for further analysis. Table 7 represents the details of the series of experiments conducted.

The input and output solid phosphogypsum and acidified filtrate of each leaching experiments were weighed and analysed for their moisture and phosphate contents.

Table 7 Details of leaching experiments of phosphogypsum

Experiment No.	Experimental Parameters			
	PG quantity (g)	Acid Concentration (%)	Gypsum (g): Acid (ml) Ratio	Process Time (Hr.)
1	100	2	100:100	1
2	75	2	75:100	1
3	50	2	50:100	1
4	100	2	100:100	2
5	75	2	75:100	2
6	50	2	50:100	2
7	100	2	100:100	3
8	75	2	75:100	3
9	50	2	50:100	3
10	100	4	100:100	1
11	75	4	75:100	1
12	50	4	50:100	1
13	100	4	100:100	2
14	75	4	75:100	2
15	50	4	50:100	2
16	100	4	100:100	3
17	75	4	75:100	3
18	50	4	50:100	3
19	100	8	100:100	1
20	75	8	75:100	1
21	50	8	50:100	1
22	100	8	100:100	2
23	75	8	75:100	2
24	50	8	50:100	2
25	100	8	100:100	3
26	75	8	75:100	3
27	50	8	50:100	3

Results and Discussions

The effect of sulphuric acid as leaching reagent for recovery of P_2O_5 from phosphogypsum is determined by investigating variables such as phosphogypsum to acid ratio - 100:100, 75:100, 50:100; acid concentration: 2%, 4% & 8%; reaction time: 60 min., 120 min. & 180 min. Material balance in terms of P_2O_5 is calculated in each case. Percentage of P_2O_5 recovered from phosphogypsum is calculated using its estimated absolute values in the initial phosphogypsum used and in the residue. Highest recovery of P_2O_5 is obtained 59.06% when phosphogypsum is treated with 4% sulphuric acid solution for 2 hours with phosphogypsum to acid ratio as 100:100. The results are given in **Table 8**.

Effect of sulphuric acid concentration on phosphorous recovery

Experiments conducted as mentioned in Table 7 shows different leaching conditions such as phosphogypsum to acid ratio- 100:100, 75:100, 50:100; acid concentration: 2%, 4% & 8%; reaction time: 60 min., 120 min. & 180 min. were employed to extract phosphorous from phosphogypsum. Leaching of the dried phosphogypsum sample with different concentration of sulphuric acid was carried out by mixing acid plus phosphogypsum with variable stirring time. Low concentration of sulphuric acid will help scavenging the P_2O_5 left in phosphogypsum [17]. At higher sulphuric acid concentrations; the efficiency of P_2O_5 leaching is decreased. **Table 8** represents the parameters and analytical data of phosphogypsum extraction experiment which gave highest P_2O_5 recovery. The effect of acid concentration, phosphogypsum: acid ratio and stirring time has found to be affecting phosphorous recovery from phosphogypsum, which is represented in **Figure 1**.

The effect of acid concentration, phosphogypsum: acid ratio and stirring time has found to be affecting Phosphorous recovery from phosphogypsum, which is represented in Figure 1.

Table 8 Parameters and analytical data of phosphogypsum extraction experiment

Concentration of sulphuric acid used		**4%**
Process Time		2 hours
Parameter	Input	Output
Phosphogypsum quantity (g)	100	86.16
Moisture in phosphogypsum (%)	20.76	11.71
P_2O_5 in phosphogypsum (%)	1.41	0.67
P_2O_5 in phosphogypsum (g)	1.41	0.57
used (ml)	245.90	250
P_2O_5 in acidified water from phosphogypsum stack (%)	0.56	0.81
P_2O_5 in acidified phosphogypsum	1.38	2.03
Total P_2O_5 (g)	2.79	2.6

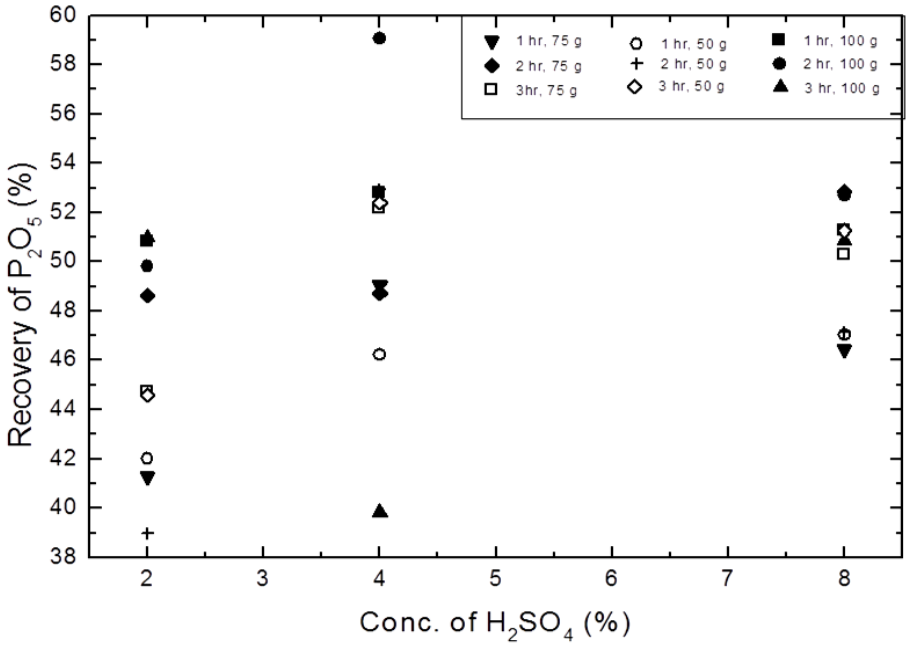

Figure 1 The effect of acid concentration, phosphogypsum to acid ratio and stirring time on phosphorous recovery from phosphogypsum

Utilisation of recovered phosphorous in phosphoric acid production

Approximately 5 tonnes of phosphogypsum is produced per tonne of P_2O_5. The degree of calcium sulphate hydration depends on the operating acid concentration and temperature [33] and may increase during transport and storage of the phosphogypsum. The dihydrate ($CaSO_4.2H_2O$) phosphoric acid process, which is the most common process to produce acid of 28-30% concentration [34]. The hemihydrate process ($CaSO_4.5H_2O$), relatively widely used in Europe, Japan and Africa produces a purer phosphoric acid product with higher P_2O_5 concentration [35]. Various modifications to the hemihydrate process have been adopted by companies to produce acid concentrations between 32% and 52%. Details of various wet phosphoric acid processes are summarized [34, 36]. The study on phosphogypsum from GSFC plant was conducted, which discusses comprehensively the R&D, manufacturing and application aspects of phosphogypsum technology [37]. Hence, the recovered phosphorous from produced phosphogypsum can be used back into the phosphoric acid production process by doing modifications in manufacturing facility which will increase process efficiency and purity of Phosphoric acid and as a result production cost will decrease and economic benefits will be achieved.

Utilisation of purified phosphogypsum in different applications

Presently, most of the phosphoric acid plants are disposing the phosphogypsum within the plant premises in stack. Depending on the demand, the phosphoric acid plants sell the phosphogypsum for different applications which

include (i) for use as soil conditioning (for alkaline soil) or as fertilizer in agriculture (ii) in cement manufacturing to control the setting time of cement (as a retardant) and (iii) small quantity is used in the production of plaster, plaster boards, gypsum fiber boards, and gypsum blocks. Utilization requires handling and transportation of phosphogypsum by means of railways or by road (mainly in trucks/tractors). The utilization of phosphogypsum depends on the degree of impurities such as fluoride, phosphoric acid and radio-activity which depends on type of raw material used in the process adopted or pre-treatment given to phosphogypsum. The method of percolation leaching with low concentration sulphuric acid solutions (~4 wt. %) for 8 hours proves effective purification of phosphogypsum of current production and stored for a long time in dumps to remove fluorine, phosphorus, heavy metals and radioactive element, making the pure phosphogypsum useful for industrial or analytical applications. For decades, phosphogypsum has been used and valued in agriculture. Positive effects of phosphogypsum are shown for soil, water and plants [38]. Phosphogypsum is mainly used in agriculture with several methods of recycling for fertilization of the soil. There are four well known agricultural uses: reclamation of land, remediation of saline and sodic soils and amendment of soil to prevent crusting and to enhance water retention, and fertilization of soil for growing crops and pasture [24]. A fifth use is also known, its addition during manure composting [39]. Indeed, Phosphogypsum is an efficient alternative for amendment, desalinization and desodification of saline sodic soils [40]. Phosphogypsum can be used as a substitute for natural gypsum in the production of Portland cement to control the hydration reaction rate of cement, but natural radioactivity of phosphogypsum would be a major disadvantage for its use as a building material. This disadvantage could be avoided by minimizing its percentage during the preparation of cement [41]. Phosphogypsum can be used for the manufacture of bricks; the incorporation of 30% phosphogypsum into the fired clay bricks provides a product which successfully satisfies standard requirements [42].

Conclusions

The optimized phosphorous leaching conditions using sulphuric acid were 4% with at 40°C temperature with a liquid-to-solid ratio of 1:1 using a 180-min reaction time. Considering the per day production of phosphogypsum of ~1000 MT, the P_2O_5 being carried away is ~13.2 MT. Even if we could recover 50% of this P_2O_5, overall efficiency of utilization of P_2O_5 in phosphoric acid production process can be increased and hence manufacturing efficiency of phosphogypsum increases. Results shows reduction of more than 50% of P_2O_5 in the residue hence recovery of phosphorous from phosphogypsum is efficient by the given process. The problem of large production, storage, and proper disposal of phosphogypsum dumps accumulated in the industries remains an unsolved issue so far. Existing phosphogypsum dumps cause pollution of the atmosphere, water bodies and soil causing alienation of soils from existing ecosystems and affecting the adjacent areas, including agricultural purposes. At the same time, these wastes have many useful components, which if recovered, can be used in various processes to increase production efficiency as well as make the gypsum stacks less polluting. Furthermore, considerable research focused on finding commercial uses for phosphogypsum can be carried out, and much more needs to be done in the future.

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